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Solid State Chemical Sensors for Monitoring Hydrogen in IOF Process Streams

**Program Review
June 6, 2001
New Orleans**

Project Team

- **Pennsylvania State University** (Nanofabrication facility) — **Mark Horn**, RaviPrakash Jayaraman, Russell Messier & Robert McGrath

- **Sandia National Laboratory (SNL)**, Combustion Research Facility — Anthony McDaniel & Dennis Morrison.

- **Air Products and Chemicals Inc. (APCI)** — Frank Schweighardt & Merrill Brenner

- **DCH Technology (DCHT)** — Peter Jardine & Dan Dunn.

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Outline

- ➢ Introduction/project Review

- ➢ Air Products & Chemicals Inc. activities

- ➢ Sandia National Labs activities

- ➢ Penn State University activities

- ➢ Project summary

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Statement of Work

Develop solid-state hydrogen sensor technology to monitor hydrogen (H_2) in IOF (Industries of the Future) process streams.

These process streams are chemically and thermally aggressive environments that may contain other reactive gases at high temperature and/or high pressure.

Background Information

- Original sensor technology was developed by Sandia Labs in partnership with Penn State.

- The technology was exclusively licensed to DCHT, who extended the development and commercialized the sensor.

- Recently advances at Sandia in active metal alloy development and in understanding of the surface chemistries governing sensor operation enable development of sensors operable in harsh, reactive chemistry environments.

- The goal of this project is to develop such advanced sensors, demonstrate their operation in IOF chemical facilities and commercialize sensors for the benefit of a large segment of the IOF chemical industry.

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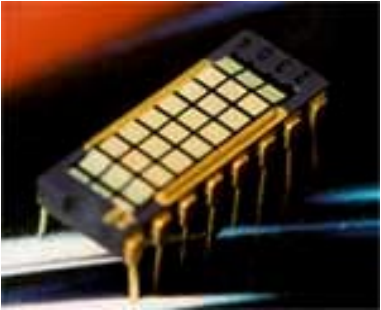
3

Project Overview

Phase I

➢ Fabricate and improve application-specific H_2 sensors.

➢ Characterize sensor response in controlled laboratory experiments involving hydrogen rich gas mixtures simulating or extracted from HyCo off-gas facilities.

➢ Conduct preliminary field tests at APCI Wilmington, CA processing plants to evaluate sensor operation in realistic industrial process environment.

Phase II

➢ Design of advanced sensor structures using theory, modeling, and experiments (SNL & PSU).

➢ Fabrication of new hydrogen sensors with advanced alloy architectures (PSU).

➢ Test prototype sensors in IOF plant environments (APCI).

➢ Transfer of technology to a commercial partner (DCHT).

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Robust Hydrogen Sensor™* from DCH Technologies

Sensor elements (resistor, transistor-FET and temperature diode) as part of an Application Specific Integrated Circuit (ASIC).

- Resistor — Pd/Ni metal strip whose resistance changes when hydrogen gets adsorbed
- FET — A Field Effect Transistor whose gate is made of a thin Pd/Ni film. The threshold voltage (voltage at which the FET turns on) changes when hydrogen is adsorbed.
- Temperature diode — A diode that monitors the temperature and maintains it at a constant value for efficient working of the sensing devices.

Sensor performance

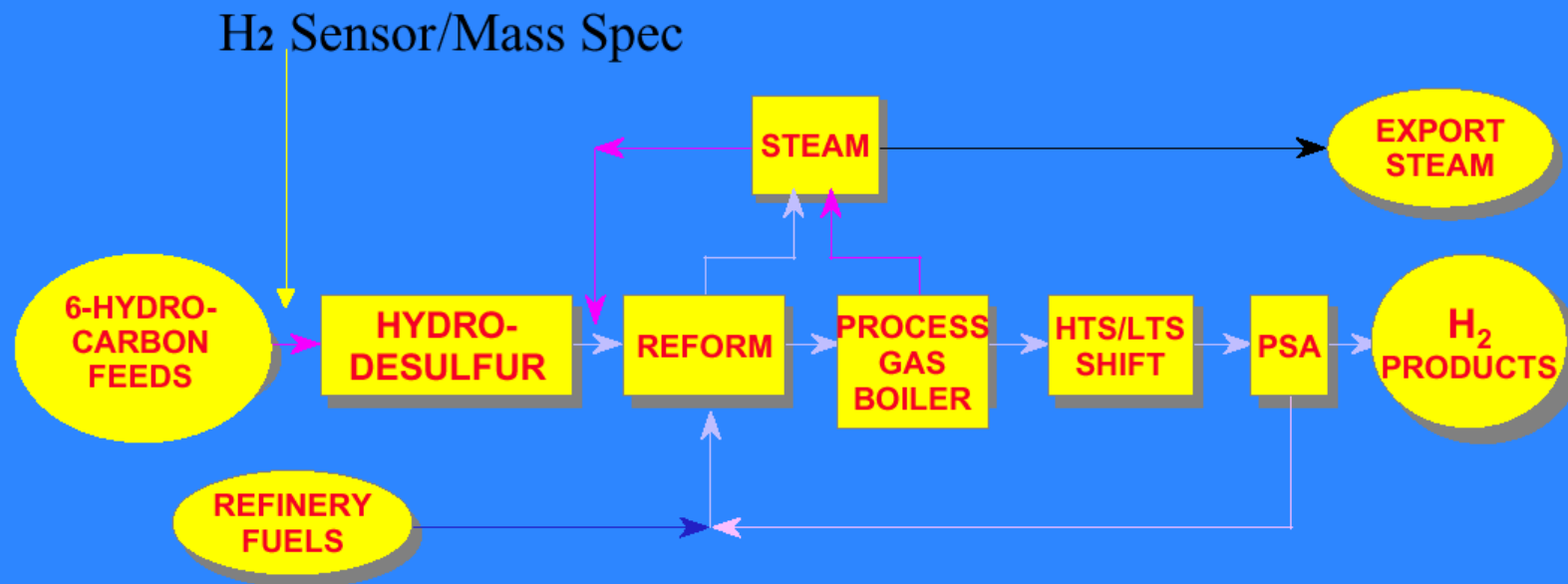|	
Measurement range	: 0 — 100% hydrogen
Accuracy	: +/- 5% depending on concentration
Operating pressure range	: tested up to 500 psi

DCHT delivered a sensor unit to APCI for field testing
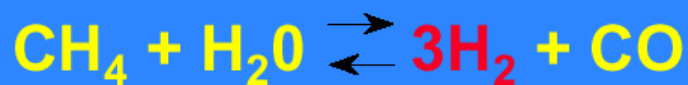
*Source : www.dcht.com/products/robust_hydrogen_sensor

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AIR PRODUCTS ACTIVITIES

**Air Products & Chemicals,Inc.
Wilmington, Ca -Hydrogen Production Site
90,000,000 SCF/day**

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HYDROGEN PRODUCTION

H₂ Sensor/Mass Spec

REFORMING

$$CH_4 + H_2O \rightleftarrows 3H_2 + CO$$

SHIFT

$$CO + H_2O \rightleftarrows H_2 + CO_2$$

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HyCO   Feed Gas Composition Analysis

Business Metric

Quantify hydrogen content in plant feedstock & in-process streams to reduce power consumption, minimize gas venting, and maximize plant performance factors.
E.G. : Reduce Steam:Carbon by 0.1 units -
Gain 1.24 BTU/SCF = 0.38% Eff
Value: 90M SCF H_2/Day * 1.24 BTU/SCF = 112M BTU/Day

Technical Metric

Incorporate on-line hydrogen analysis time to <5 sec; improve compositional analysis accuracy (<0.1%) and, reduce cost per analysis by 38%.

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ABB/EXTREL
Process Mass Spectrometer ($165,000)
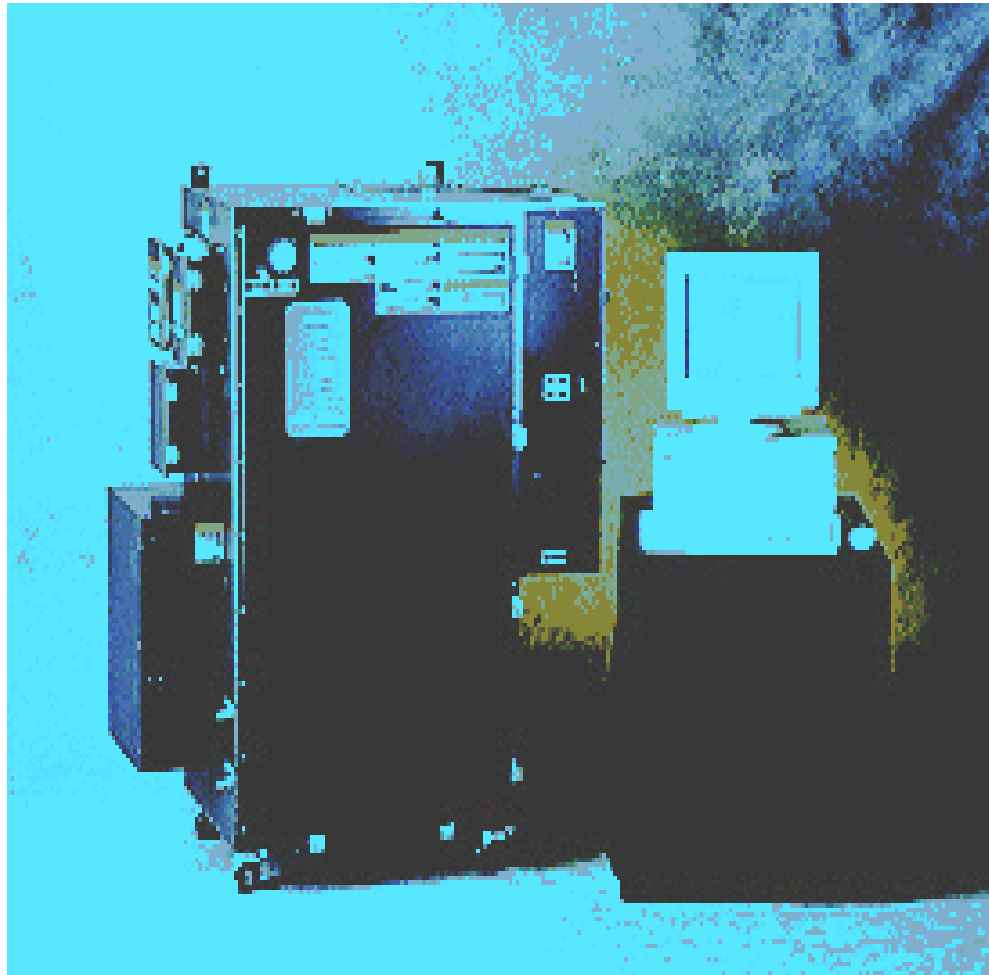
Mass Spec -HyCO Feed Analysis

9.5

8.5

Hydrogen Content - Feed

9.23%

3150

3000

3050 BTU/SCF

Feed Gas - BTU/SCF

87.2
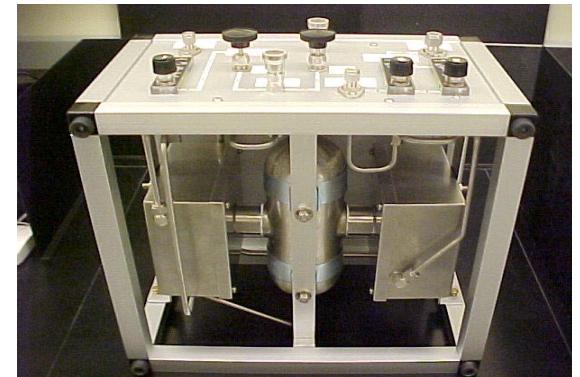
86.1%

Methane Content - Feed
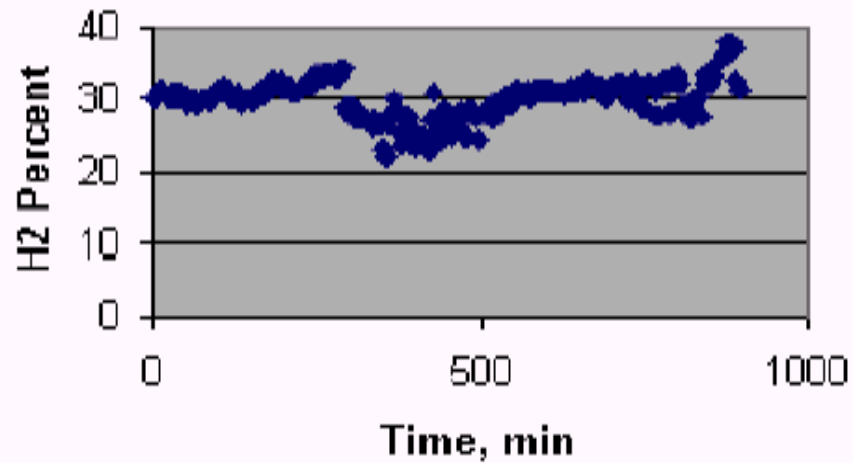
0   15   30   45   60

Time, min
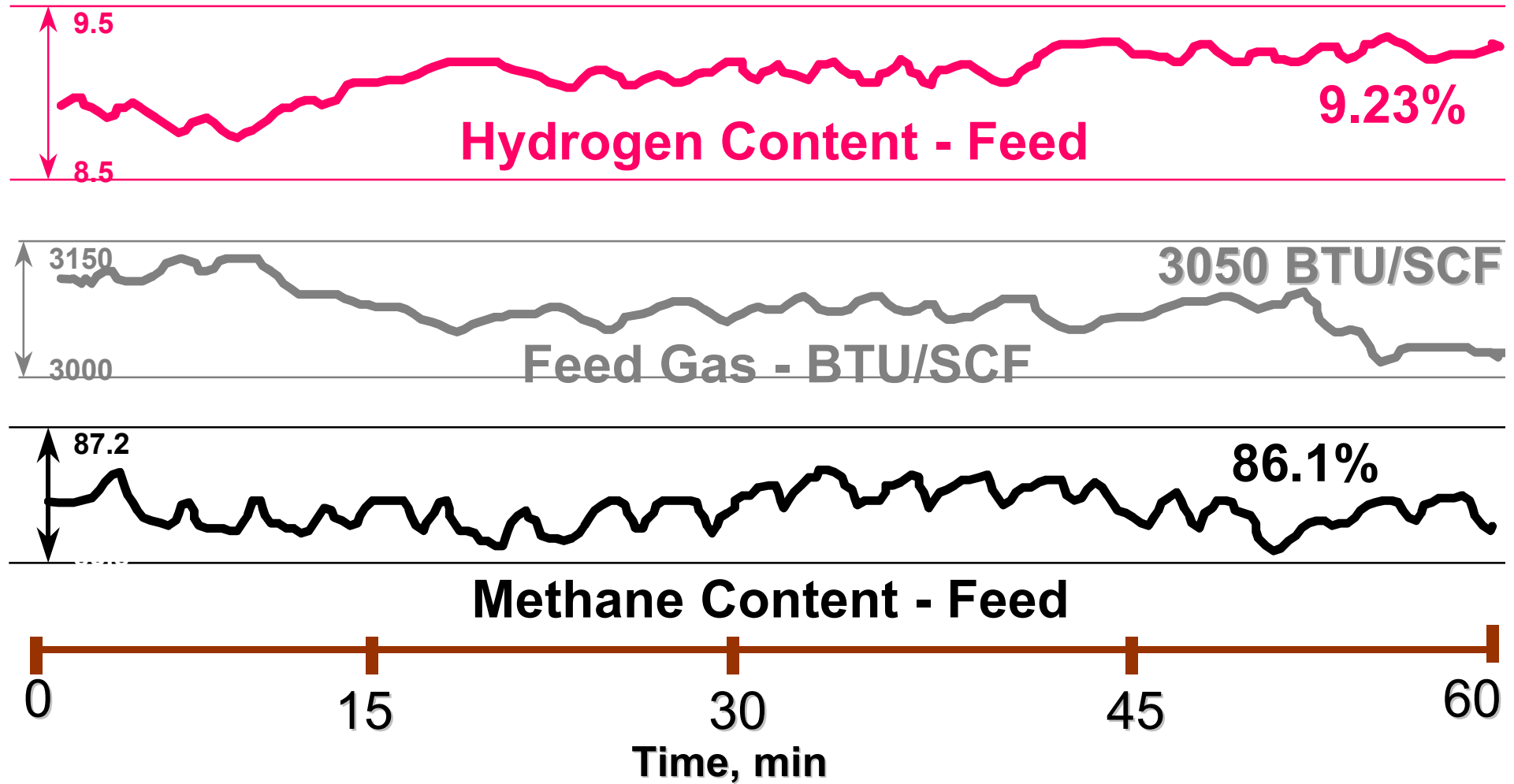
Process Testing protocol

- Design/construct Hydrogen sensor test assembly

- Complete hazard review

- System

    o 1-liter stainless steel flow vessel

    o Two DCHT sensors facing each other

    o Purge rate — 5 liters/minute at 25 psi

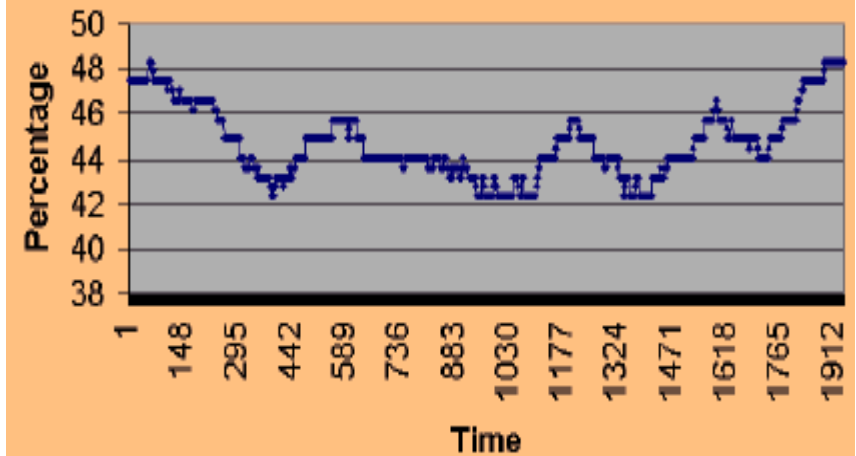   o Interface with HyCO feed (before mass spec)

- Test phase 10 days

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Measured variation in Hydrogen content in feed gas

Mass spectrometer

DCHT sensor

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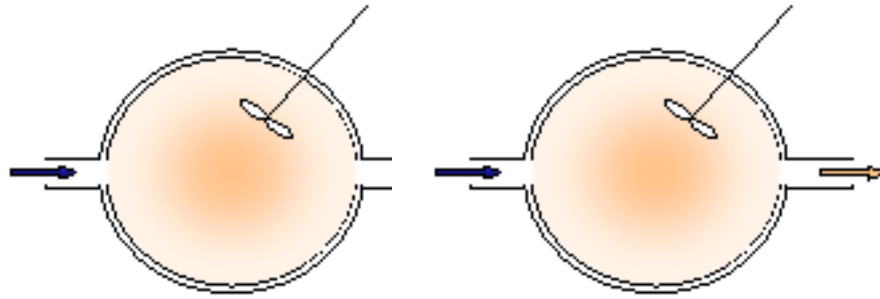Combustion Research Facility

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Summary

- ➢ Current technology (DCHT sensor) adequate for remote monitoring on extracted samples
  - Needs to be pressure compensated and temperature controlled
  - Sample line preconditioned, unclear as to the effects of poisoning or chemical interference

- ➢ APCI not interested in replacing mass spectrometers with H_2 sensors

- ➢ Industry desires in situ process monitors
 - Survive aggressive process environments at low cost

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SANDIA ACTIVITIES

- Theoretical tools for predicting sensor behavior
  - Modeling tools for simulation-based data reduction and optimization of sensor performance
  - Elementary reaction mechanisms for describing relevant chemistry at the gas-sensor interface
  - First-principles description of the sensor response function as it relates to surface coverage of hydrogen

- Experimental apparatus for evaluating sensor behavior
  - Characterize sensor in laboratory setting under process-like conditions
  - Identify hostile operating conditions that lead to device failure
  - Evaluate new sensor designs

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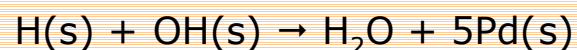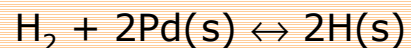# Modeling Tool Used to Simulate Device Behavior

$$\rho V \frac{dY_k}{dt} = \dot{m}^* (Y_k^* - Y_k) + \dot{\omega}_k W_k V + \sum_{m=1}^{M} \dot{s}_{k,m} W_k A_m - Y_k \left(\sum_{m=1}^{M} A_m \sum_{j=1}^{K_g} \dot{s}_{j,m} W_j + \rho V \left(\frac{1}{T} \frac{d\overline{T}}{dt} - \frac{1}{\overline{W}} \frac{d\overline{W}}{dt} \right) \right) \qquad k = 1, \dots, K_g$$

$$\rho V \left(\overline{c}_p (1 - Y_e) \frac{dT}{dt} + Y_e c_{pe} \frac{dT_e}{dt} \right) = \dot{m}^* \sum_{k=1}^{K_g} Y_k^* \left(h_k^* - h_k \right) - V \sum_{k=1}^{K_g} h_k \dot{\omega}_k W_k - \sum_{m=1}^{M} A_m \sum_{k=1}^{K_{tot}} h_k \dot{s}_{k,m} W_k - Q_{loss} - Q_{source}$$
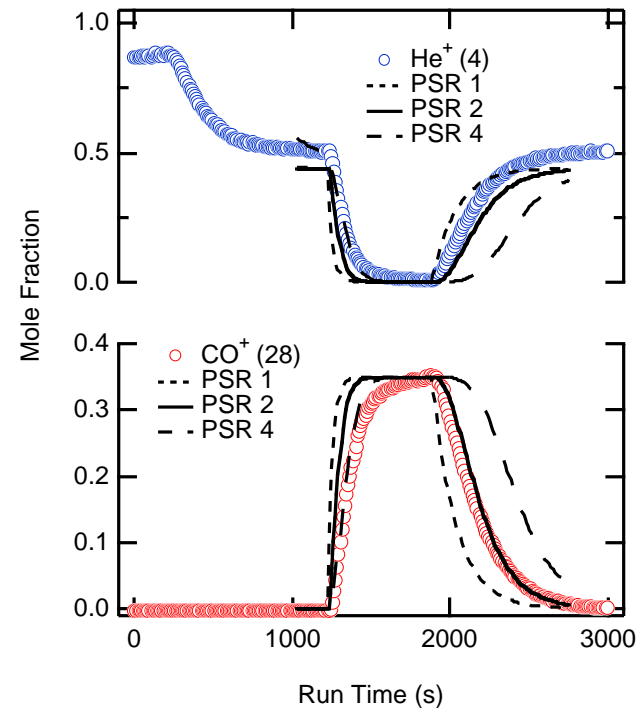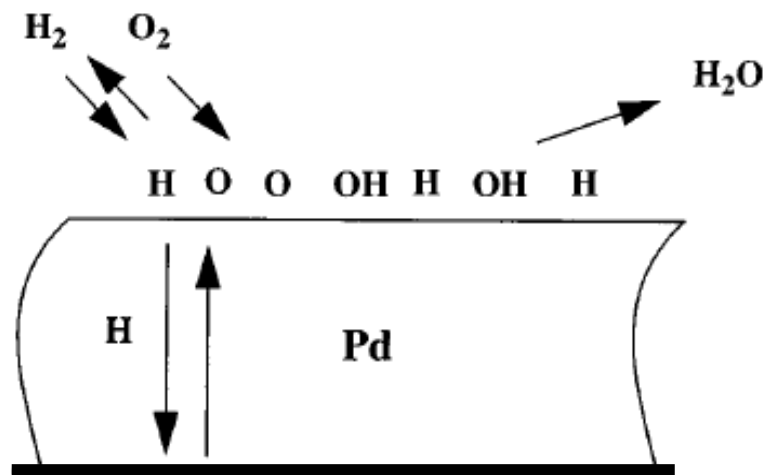
- Transient Continuously-Stirred Tank Reactors (TCSTR) model used to predict behavior of H_2 sensor in different chemical environments
  - Model experimental data, resolve key kinetic parameters
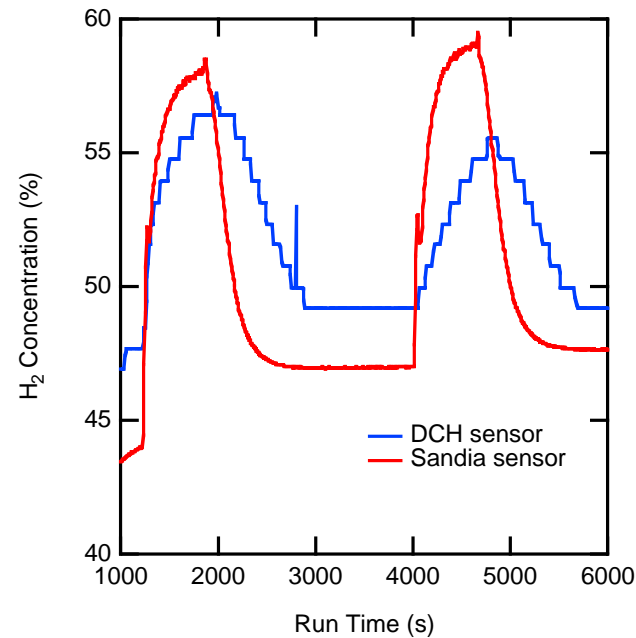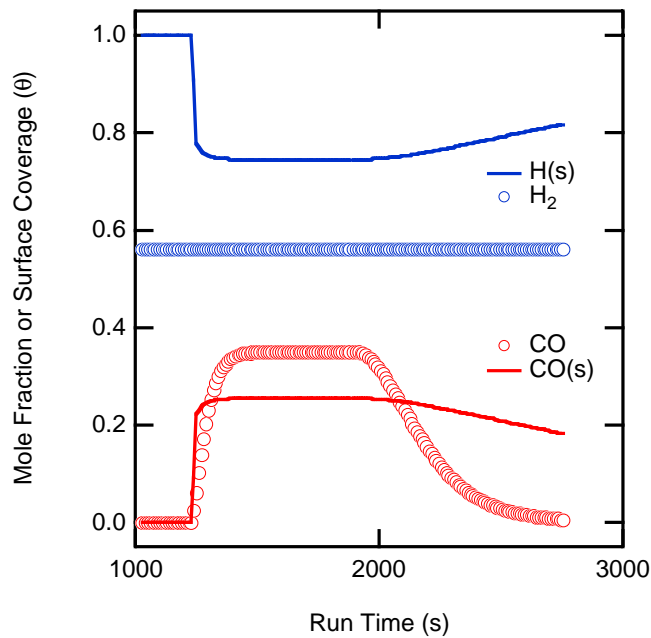
Sample Reaction Mechanism for Pd / H_2 / O_2 System

$H_2 + 2Pd(s) \leftrightarrow 2H(s)$

$O_2 + 8Pd(s) \rightarrow 2O(s)$

$H(s) + O(s) \rightarrow OH(s) + Pd(s)$

$H(s) + OH(s) \rightarrow H_2O + 5Pd(s)$

H diffuses into bulk Pd

- Reaction sequence describes:
  - Adsorption of H_2 and O_2 to form the adatoms $H(s)$ and $O(s)$
  - Reactions between adsorbates to create surface bound $OH(s)$ and H_2O
  - Coverage of $H(s)$ determines the bulk H content of the film
  - Evaluate the effects of CO and H_2S exposure

- Kinetic parameters for surface reactions available in literature or can be determined experimentally via model-based data reduction methods

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# H₂ Surface Coverage and Sensor Response

- Conditions of numerical experiment
- H_2:He (56%:44%) exposure followed by HyCO gas matrix (56% H_2, 35% CO, 5% CO_2, 4% CH_4)
- T_{gas} = 300 K, $T_{surface}$ = 353 K

- CO able to adsorb onto H(s)-covered Pd surface, inhibit H_2 reaction, predict relatively long recovery times

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Device Characterization

- Laboratory facility
  - Expose test structures to controlled environments (temperature, pressure, gas composition)
  - Residual gas analyzer (RGA) used to monitor gas composition of sensing environment
  - Employ rapid-screening techniques, simultaneously monitor ΔR from all 12 resistor elements with custom hardware, electronics, and LabView software

- Use design of experiment (DOE) methods to plan and coordinate research activity

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Data/Results Sandia sensor

- **Quadratic dependence in terms of total pressure and H$_2$ concentration**

- **Observed response in good agreement with theory**
  - Sievert's Law
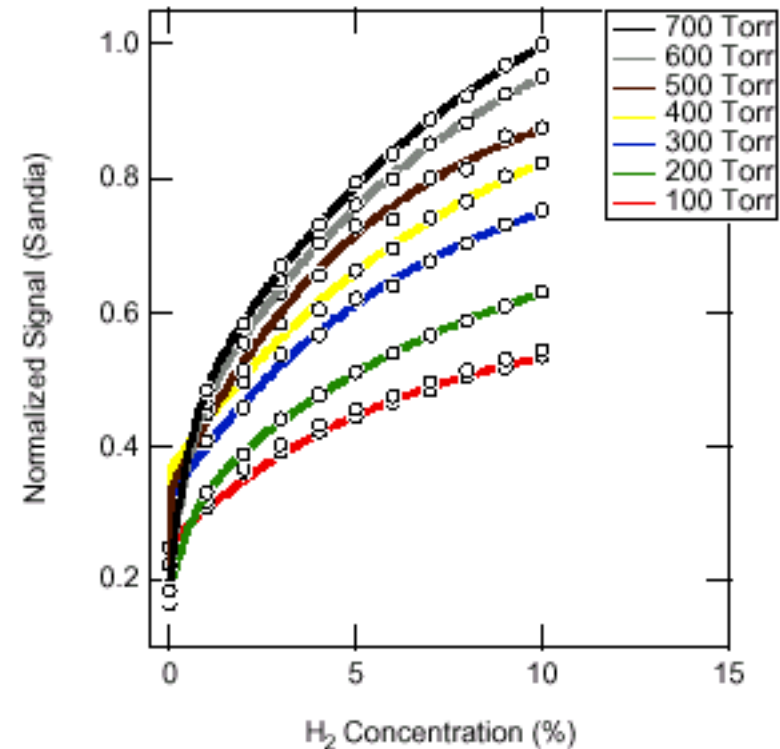
- DCH sensor exhibits a linear response to H_2 concentration and total pressure

- Behavior of Sandia and DCH sensors are not consistent

- WHY?
  - DCH manipulates electronic signal differently
  - Possible effects on sensitivity or system response
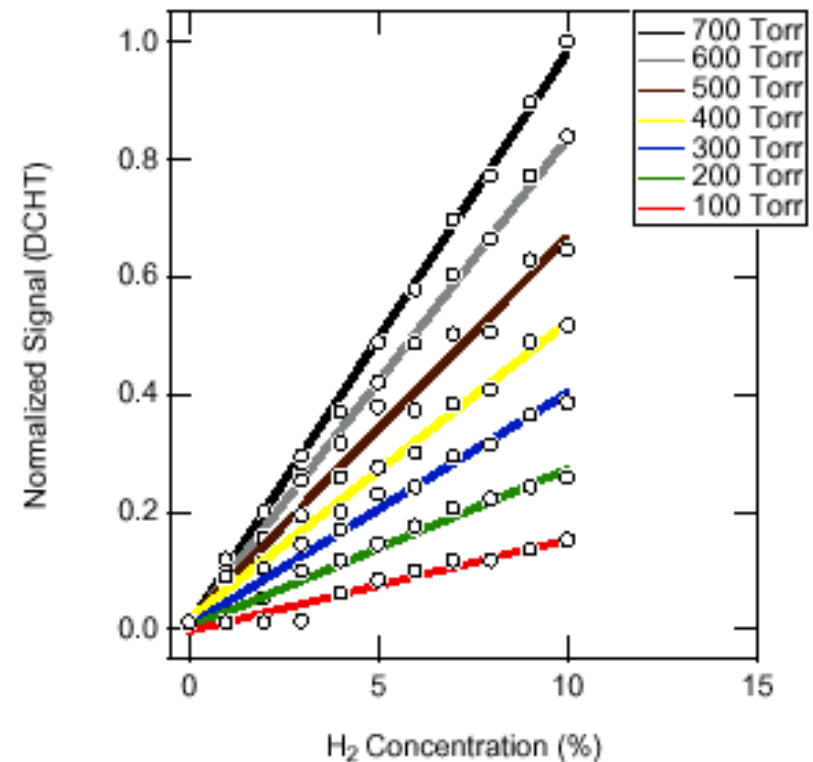
Summary

➢ Developed numerical model of sensor behavior
  • Includes detailed surface chemistry
  • Use model predictions to design high pressure experiments and survey potential alloy partners for Pd

➢ Sandia and DCHT sensors differ in response characteristics to H_2
  • DCHT post processing of ΔR corrects for non-linear physics
  • Sensors must be pressure compensated to recover absolute H_2 concentrations

➢ Evaluated Sandia and DCHT sensors in HyCo mixtures
  • Evidence of reduced sensitivity after CO exposure

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PENN STATE ACTIVITIES

➢ Resolve processing issues in metallization (Pd/Ni alloys)
  - Sputter deposition of Pd/Ni alloy films
  - Pattern metal films using lift-off process
  - Establish metal film composition using resistivity and EDS measurements

➢ Design and fabricate sensors and provide prototype for characterization and testing at SNL
  - Incorporate advanced active metal alloys (Phase I)
  - Evaluate processes and performance of chemiresistors

Status at last Program review (Baltimore - 06/00)

➢ Optimize metal deposition procedure (magnetron sputtering) to deposit alloys and alter alloy compositions

➢ Initiate mask design based on Sandia sensors — chem-resistors

Current status (New Orleans - 06/01)

➢ Established process flow for fabrication of sensors

➢ Finalized design of sensor and fabricated masks

➢ Fabricated sensors with different alloy compositions (to be tested)

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Design considerations for fabrication of chemiresistors

Design considerations
- Stability, reproducibility, response time and recovery.

Effects
- Joule heating
- alloy composition.
- structure — microstructure, morphology.
- geometry — perimeter to area ratio, edge to area ratio, active to non-active area, film thickness.
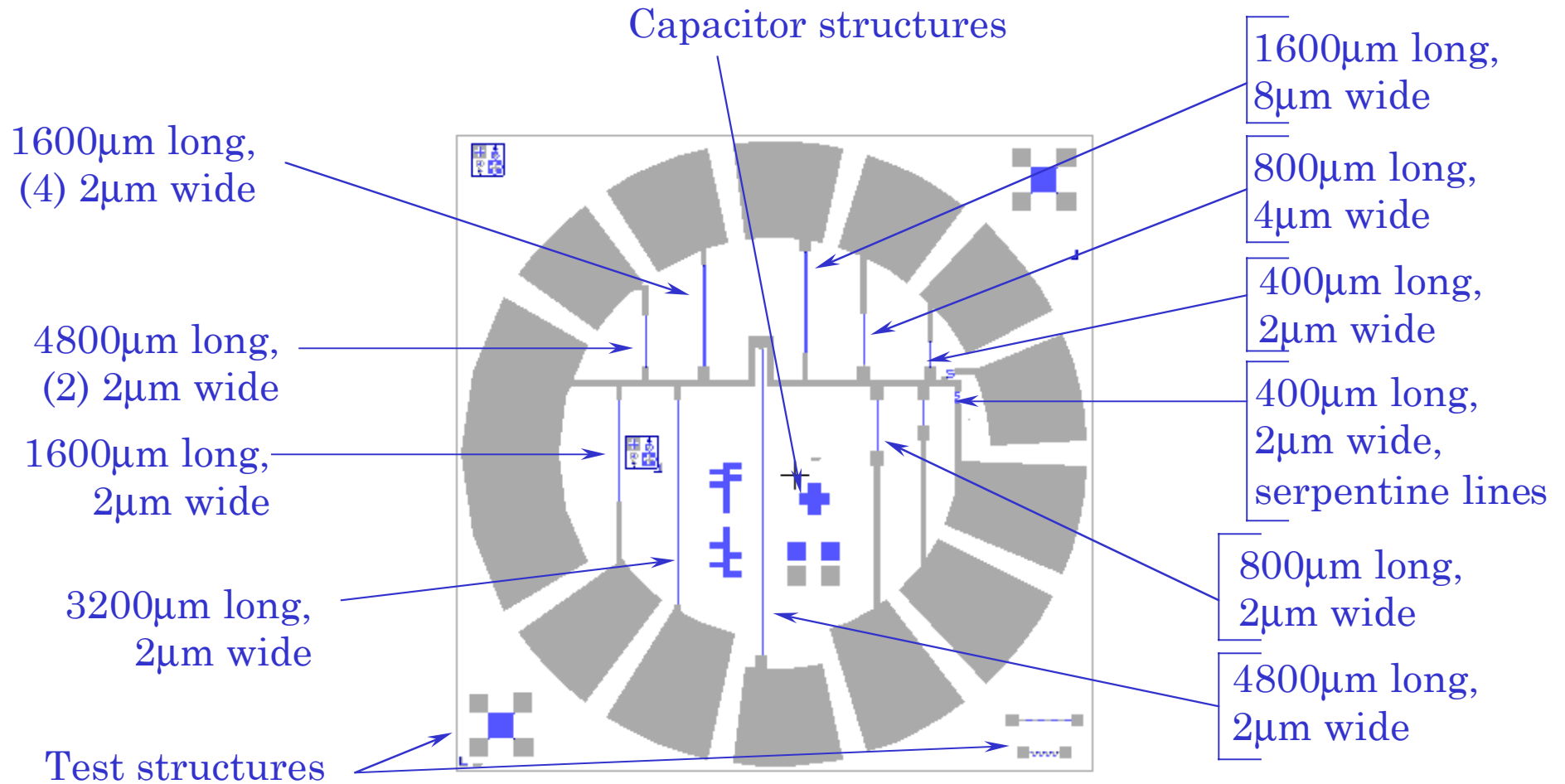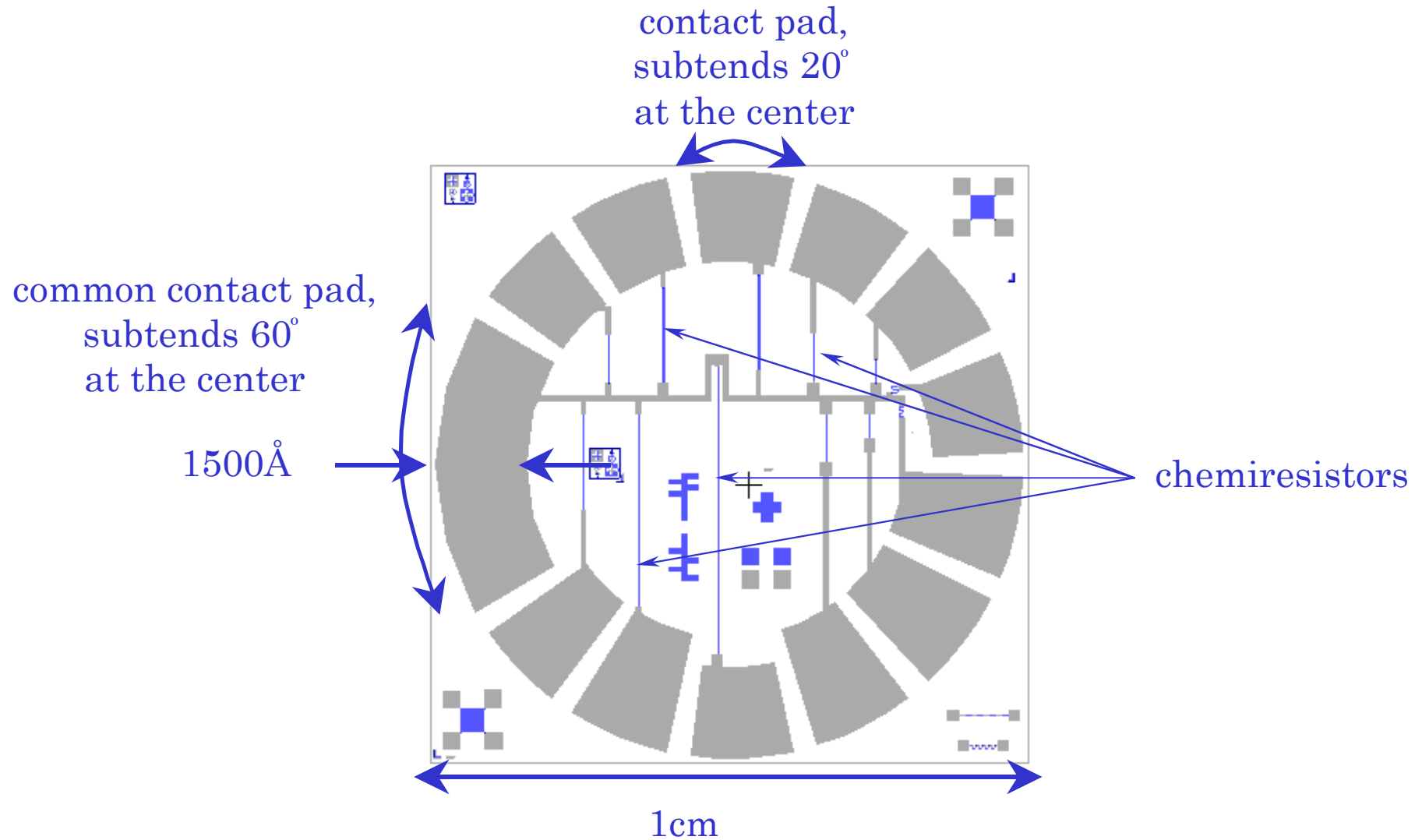
Chemiresistor structure

simple Resistor

active/non-active area

perimeter/area

edge/area
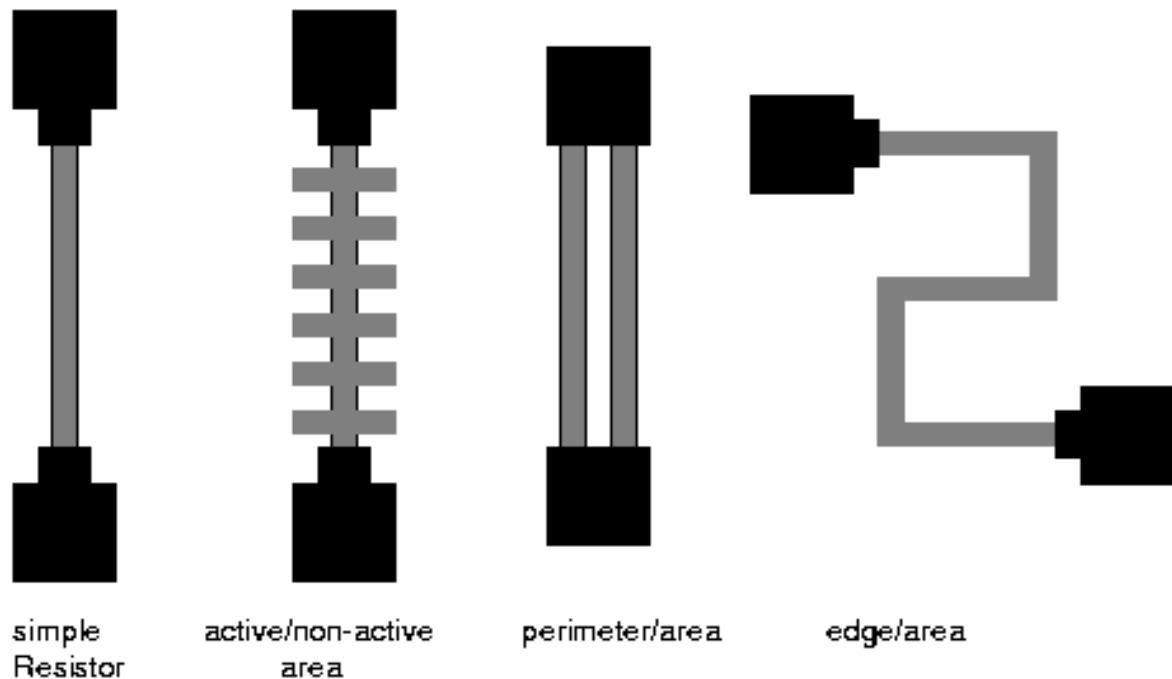
Parameters chosen

- Resistance — 500 to 5000 Ω (length - 400µm, 800µm, 3200µm, 4800µm)
- Film thickness — 500 to 2500 Å
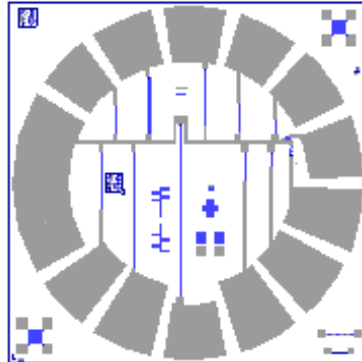
Chemiresistor – individual die

Capacitor structures

1600μm long,
8μm wide

800μm long,
4μm wide

400μm long,
2μm wide

400μm long,
2μm wide,
serpentine lines

800μm long,
2μm wide

4800μm long,
2μm wide

1600μm long,
(4) 2μm wide

4800μm long,
(2) 2μm wide

1600μm long,
2μm wide

3200μm long,
2μm wide

Test structures

Chemiresistor – individual die

contact pad,
subtends 20° at the center

common contact pad,
subtends 60° at the center
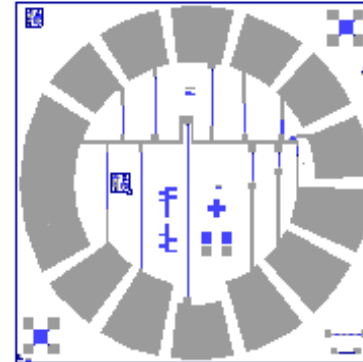
1500Å

1cm

chemiresistors

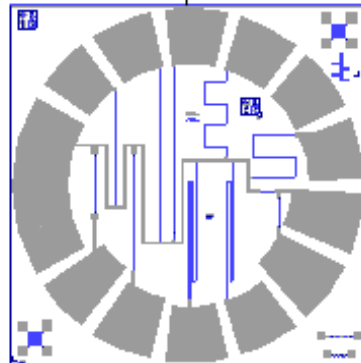# Chemiresistor mask layout
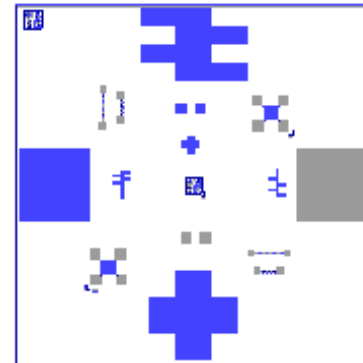
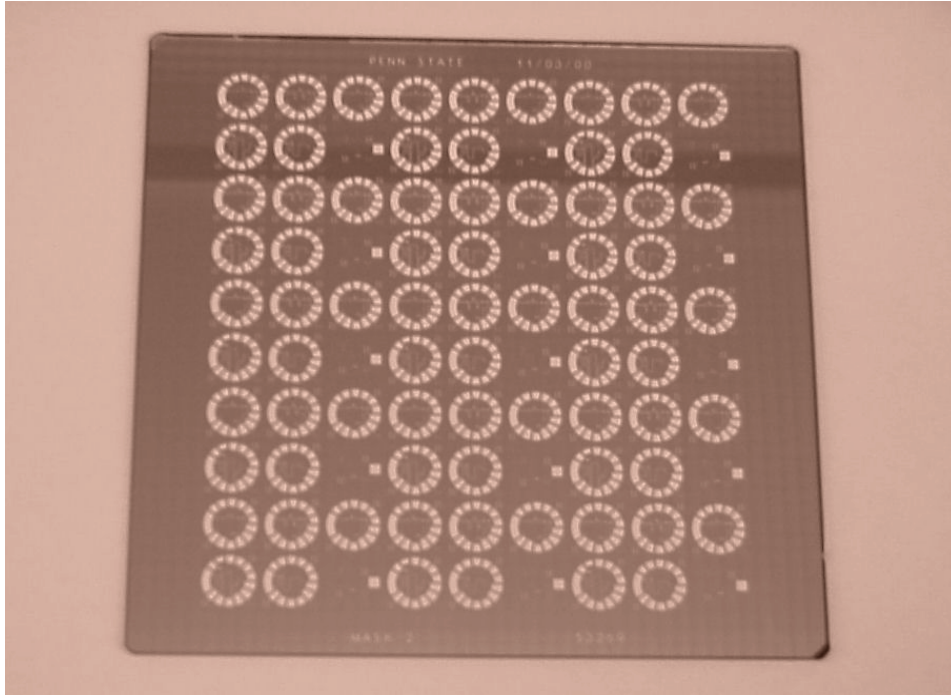400μm lines   800μm lines   1600μm lines
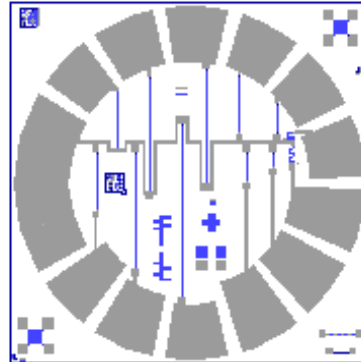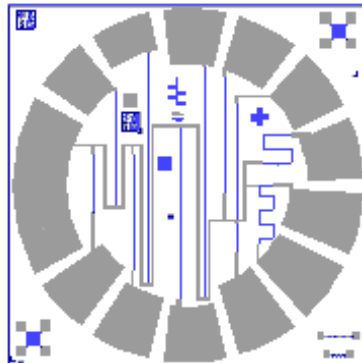
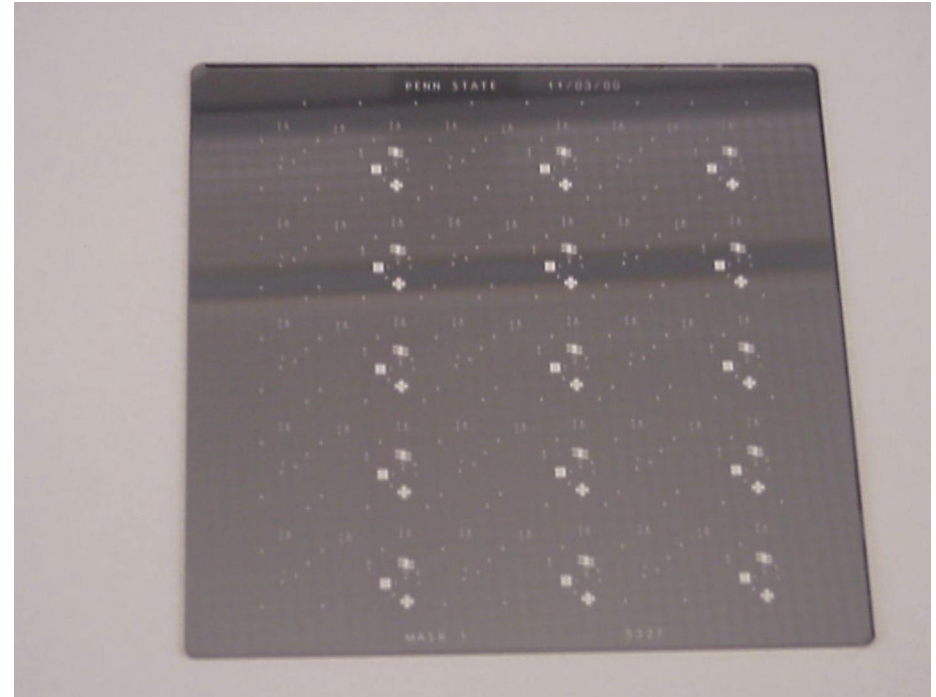

3200μm lines   4800μm lines   Test structures
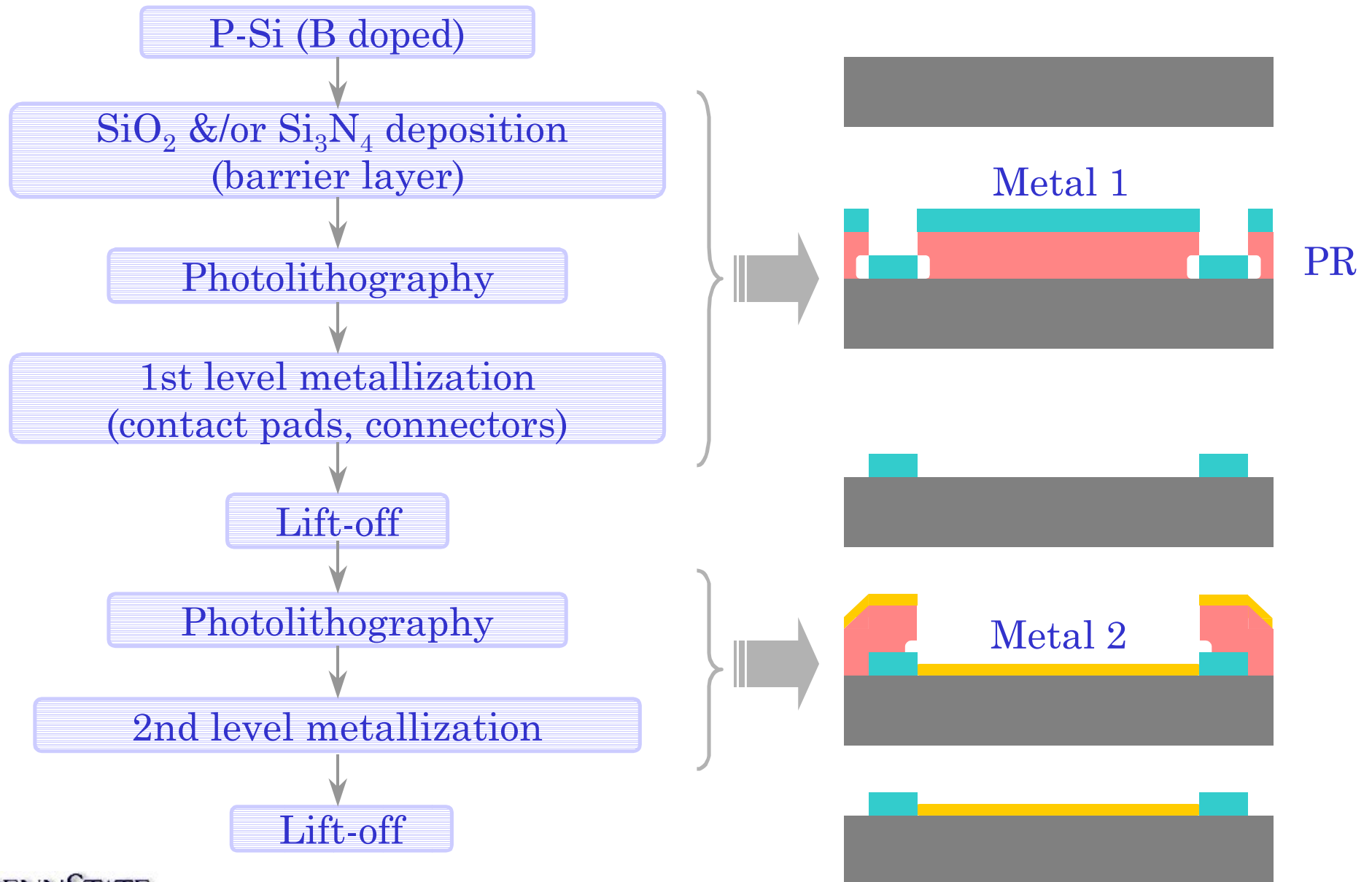
Chemiresistor masks

Mask 1

Mask 2

Mask 1 – contact pads and interconnects.

Mask 2 – chemiresistors (Pd/Ni alloy metal lines)

Process Flow

P-Si (B doped)

↓

SiO$_2$ &/or Si$_3$N$_4$ deposition
(barrier layer)

↓

Photolithography

↓

1st level metallization
(contact pads, connectors)

↓

Lift-off

↓

Photolithography

↓

2nd level metallization

↓

Lift-off

Metal 1

PR

Metal 2

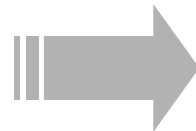# Photolithography — 2 step process

Spin on Shipley 1813

Soft bake 115°C, 45 sec

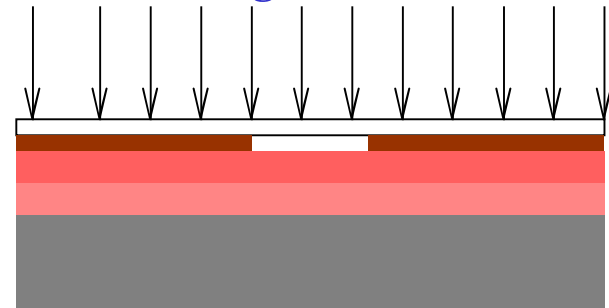5 min Chlorobenzene soak

Exposure with mask

Develop,
Postbake at 115°C, 10 min

PR

UV light

mask
PR

Metallization

Contacts (evaporation)
200Å Ti (e-gun evaporation) + 1000Å Al

Resistor lines (magnetron sputtering)

200Å Ti + 200Å Ni (e-gun evaporation)
+
1000Å Pd/Ni (5 min)

Sputter deposition conditions

Pd – 20 W power, 5 mTorr pressure
Ni – 20 W power, 5mTorr pressure
frequency   = 440 kHz
pulse width = 145 μm

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Schematic of magnetron sputter deposition system

DC source

Pulsed DC source

Pd

Ni

Hiden probe (energy analyzer, mass spectrometer)

Cryo pump

Sample holder

shield

View port

Top view
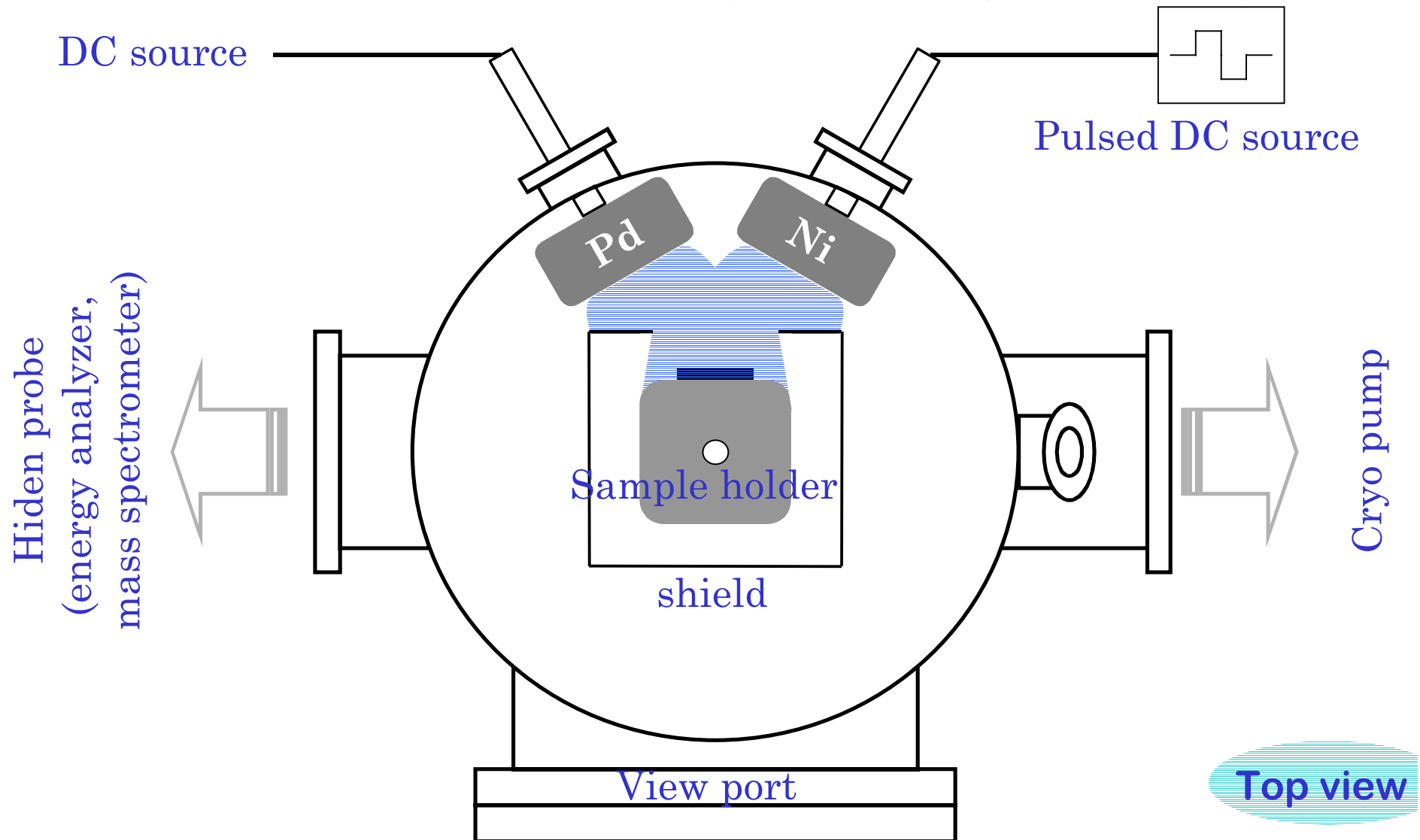
Chemiresistor structures
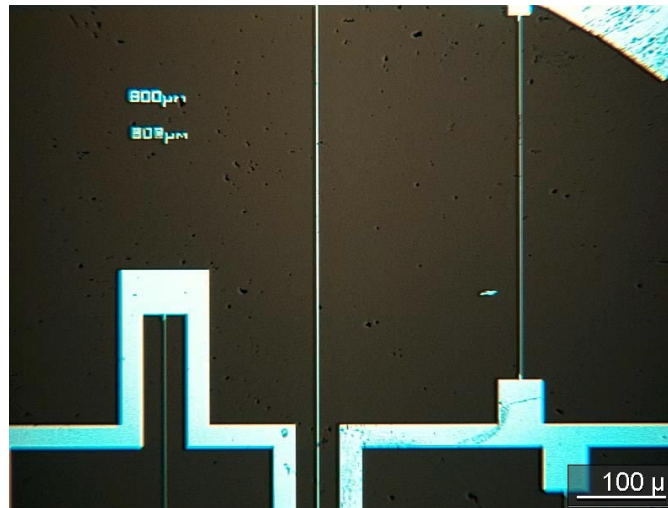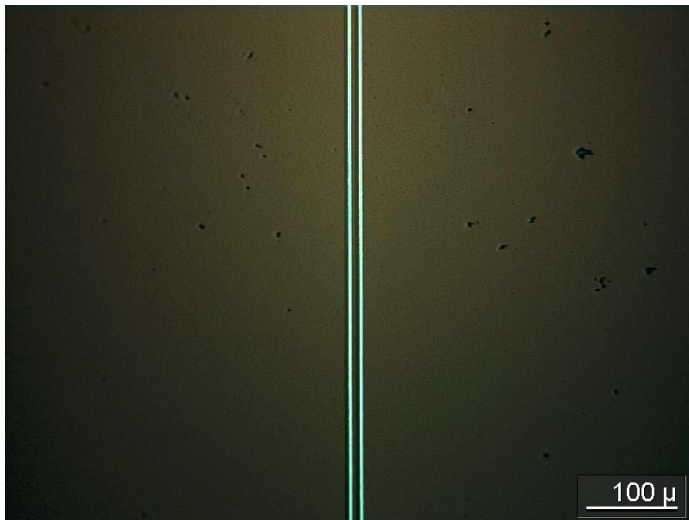
Budgetary Summary for Phase I and Phase II (projected)

	Phase I	Phase II (year 1)	Phase II (year2)
DOE Funds	100,000	400,000	400,000
Cost Share	75,515	147,754	144,152
Annual Totals	175,515	547,754	544,152
Total Project			1,267,421

Notes: Project includes research and demonstration activities in each project year reflecting deployment and, hopefully, commercialization of incremental improvements in hydrogen sensor technology. Appropriate cost sharing is provided in all cases.

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Project Schedule — Phase I

Activity Name	Start Date	Finish Date	FY 00	FY 01
			D J F M A M J J A S	O N D J F M
Phase I:				
Award announced via OIT internet site	12/15/99			
Contract negotiations with Chicago Field Office	2/1/00	9/1/00		
Task Ia: Sensor Fabrication (PSU)				
Procure DOE funding / Official start date of project	9/1/00			
Adapt electronic fabrication facilities to reproduce Sandia / DCHT technology at PSU	7/1/00	11/1/00		
Fabricate H2 chemiresitor	7/1/00	1/1/01		
Establish fabrication protocols at PSU for altering alloy composition	9/1/00	1/1/01		
Task Ib: Sensor Characterization (SNL)				
Procure DOE funding	6/1/00			
Procure test equipment from DCHT	7/1/00			
Construct lab facility for sensor testing	5/1/00	11/1/00		
Characterize Sandia chemiressitor in high H2 and HyCO test-gas matrix	3/1/00	12/31/00		
Characterize DCHT chemiressitor in high H2 and HyCO test-gas matrix	11/1/00	12/31/00		
Characterize PSU fabed chemiressitor in H2 and other test-gas matrices	1/1/01	3/1/01		
Task Ic: Field Tests (APCI)				
Procure test equipment from DCHT	7/1/00			
Prepare, test, and document DCHT sensor/process interface at APCI Allentown, PA prior to field trial	7/1/00	9/1/00		
Test window for H2 sensor at HyCO facility (Wilmington, CA)	9/1/00	11/1/00		
Analyze field data and prepare report	11/15/00	3/1/01		
Administrative Activities				
DOE program review meeting in Baltimore, MD	6/6/00			
On-site group meetings between PSU, SNL, APCI, & DCHT	1/27/00 9/29/00			
Revise Phase II program plan	2/1/01	3/1/01		
Chemiresistor: proceed with Phase II activites	4/1/01			
			D J F M A M J J A S	O N D J F M

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Project Schedule — Phase II

Activity Name	Start Date	Finish Date	FY 01	FY 02
			A M J J A S O N D J F M A	
Phase II (24 months)				
Task IIa: Design of advanced sensor structures (SNL)				
Model existing sensor chemistry	4/1/01	10/1/01		
Develop surface-chemistry models for alternative sensor materials	10/1/01	10/1/02		
Predict effects of mixed IOF gas streams on sensor performance	4/1/01	10/1/02		
Select improved sensor designs	7/1/01 1/1/02 7/1/02			
Prepare specifications for new sensor designs	7/1/01 1/1/02 7/1/02	9/1/01 3/1/02 9/1/02		
Lab characterization of fabricated sensors	9/1/01	1/1/03		
Task IIb: Fabrication of new sensors with advanced properties (PSU)				
Fabricate chemiresistors	7/1/01 9/1/01	10/1/02		
Performance qualification	3/1/02 10/1/02			
Fabricate multiple-element sensors	4/1/02 8/1/02	1/1/03		
Performance qualification	1/1/03			
Incorporate H2 selective membranes into sensor designs	4/1/02 8/1/02	1/1/03		
Performance qualification	1/1/03			
Task IIc: Prototype testing in IOF plant environments (APCI)				
Prepare test unit for plant installation	8/1/01	10/1/01		
Plant testing (high H2)	10/1/01	12/1/01		
Prepare test unit for specialty chemical plant installation	3/1/02	5/1/02		
Plant testing (specialty chemicals)	5/1/02	7/1/02		
Delivery of plant testing data to SNL and PSU for analysis	12/1/01 7/1/02			
Task IId: Transfer technology to commercial partner				
Prepare specifications for commercial sensors	8/1/02	3/1/03		
DCHT, design process interface for next generation devices	8/1/01	3/1/03		
Final report	4/1/03			
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Milestones Achieved

➢ Established sensor fabrication protocols at PSU and fabricated sensors

➢ Delivery of DCHT sensors and control unit to APCI, PSU, and Sandia

➢ Setup sensor characterization facility at SNL and tested DCHT, Sandia, and initial PSU sensors

➢ Evaluated DCHT and Sandia sensors in HyCo gas test matrix

➢ APCI field tested DCHT sensors at HyCo facility at Wilmington, Ca

Future Work

➢ Extensive investigation of current PSU test structures (Pd and Pd/Ni) at high temperature, high pressure, and HyCo gas ambients

➢ Investigate viability of various alloy metals (Ag, Sn, Cu, ?) with Pd

  • Prevent H_2-induced phase transition in Pd at high pressure

  • Control undesirable surface chemistry

➢ Fabricate and test resistor structures with different alloy compositions

➢ Investigate selectively permeable coatings to protect active surface from chemical poisoning (sulfur compounds)

➢ Construct high pressure testing station for characterizing sensors under more process-like conditions

➢ Additional field trials at HyCo and other chemical plants

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AIR PRODUCTS

Sandia National Laboratories
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DCH TECHNOLOGY